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Interactive Comment

Interactive comment on "Thermodynamics of homogeneous nucleation of ice particles in the polar summer mesosphere" *by* A. Y. Zasetsky et al.

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1 General remarks

There is an evidenced need to reconsider ice formation in the mesosphere (cf. Specific comments). The authors proposed homogeneous nucleation as a mechanism of ice nano-particle formation in the polar summer mesosphere. The key idea is the replacement of the capillarity approximation (CAP) by considering the curvature dependence of the surface tension. The approach presented here is both physically sound and stringent. Both scientific significance and quality of the paper are evaluated as excellent. I recommend the paper for publication in ACP after minor revisions.

2 Specific comments

Noctilucent clouds (NLCs) are conspicuous and fascinating phenomena, being the highest clouds in Earth's atmosphere. These clouds are hypothesised to be formed by water vapour condensation to ice particles at very low temperatures. Favoured conditions for their formation are given at altitudes of around 75 to 85 km in the mesosphere, especially over the North Pole in the summer, when mesospheric temperatures can fall below $-140\,°C$. NLCs are also known as polar mesospheric clouds (PMCs), which can cause strong radar echoes, known as polar mesosphere summer echoes (PMSEs) (e.g., Berger and Lübken, 2006). The interrelations between NLCs/PMCs and PMSEs are not fully understood and subject of ongoing research. Ice particles may serve as effective sinks for ablation products of meteoroids, such as potassium. In view of the extremely low water vapour content in the mesosphere and owing to the strong limitation of direct observations, there is still some debate on the mechanism of ice formation in the mesosphere (but not only there). In this context, Frank's aphorism "Of all known liquids, water is probably the most studied and least understood" can be claimed truth as in 1972, when it was spoken out.

Due to the lowering of the critical formation energy by the activity of a foreign substrate with respect to nucleation catalysis, heterogeneous nucleation of water vapour on pre-existing particles is favoured over homogeneous nucleation of pure water vapour to form ice. In the mesopause region tiny particles of meteoric origin are supposed to serve as condensation nuclei for heterogeneous ice formation, thus contributing in some way to NLC formation. According to the classical understanding, most of the meteoric material entering the Earth's atmosphere evaporates at 80–100 km altitude. At these altitudes the characteristic temperature of the meteoric material exceeds ≈ 2100 K as a result of deceleration (aerodynamic drag) of meteoric material, leading to evaporation. Much of the refractory vapour quickly recondenses into a multitude of tiny particles, whereas the recondensation process is considered to perform in two steps:

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(a) oxidation of meteoric materials, such as Fe and Si, by collision with atmospheric O_2 to form FeO and SiO_2; (b) subsequent collision of the oxidised materials with each other to form larger smoke particles. Meteoric dust formation is assumed to be a barrierless process, because the equilibrium vapour pressures of FeO and SiO_2 are quite low even at elevated temperatures. Thus, two colliding molecules should not encounter an energy barrier to nucleation (Hunten et al., 1980).

Presuming the abundance of pre-existing particles, originating from recondensation of vapourised meteoric ablation products, heterogeneous nucleation is a very plausible mechanism of ice formation in the mesopause region. Formation of icy particles by heterogeneous nucleation on nanometer-sized CNs is considered in various modelling studies, such as those performed by, e.g., Rapp et al. (2003), Berger and Lübken (2006), Berger and v. Zahn (2007), and Raizada et al. (2007). The evolution of meteoric dust CNs has been modelled by Bardeen et al. (2008). In the context of the ice formation mechanism, the following defiances are posed:

- Current microphysical models were found do not satisfactory describe PMSE physics and are needed to be improved (Rapp et al., 2003).
- NLCs can be observed at mesopause temperatures, which are much too large for ice particles (Berger and Lübken, 2006, cf. references therein).
- Berger and v. Zahn (2007, cf. references therein) based their calculation on a CN size distribution, which is characterised by comprising only particles with radii between 1.0 and 3.5 nm. This choice was motivated, among others, by the fact, that ice nucleation on smoke particles with radii < 1.0 nm is very unlikely.
- If smoke particles of meteoric origin are the only nucleation kernel for ice in the mesosphere, this would imply, that there could only be of the order of 100 or less ice particles cm^{-3} at the Arctic summer mesopause, which is much less than the

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ice number densities expected for the formation of ice phenomena, such as NLCs and PMSEs (Megner et al., 2007).

Against this background the authors proposed the hypothesis, that also homogeneous nucleation is a possible mechanism of ice nano-particle formation in the polar summer mesosphere. Here is my evaluation of the manuscript:

1. The manuscript represents a substantial contribution to scientific progress within the scope of ACP. It presents a hypothesis of homogeneous nucleation of ice nano-particles in the polar summer mesosphere.

2. To support their hypothesis the authors employed new satellite-based data, classical nucleation theory (CNT), classical concepts of thermodynamics (Oswald's step rule) and nonclassical methods to overcome the capillarity approximation in the CNT by considering the curvature dependence of the surface tension. As the parameters controlling the curvature dependence of the surface tension cannot be derived within the framework of classical thermodynamic theory (Tolman, 1949) or by direct measurements, alternative approaches have to be employed such as molecular dynamics (MD) simulations and density functional theory (DFT), respectively (e.g., Baidakov and Boltachev, 1999, Baidakov et al., 2000, Baidakov and Boltachev, 2005, Boltachev et al., 2003, Boltachev and Baidakov, 2004a, Boltachev and Baidakov, 2004b, Bykov and Shchekin, 1999, Fokin and Zanotto, 2000, Fokin et al., 2000, Fokin et al., 2006, Hamill et al., 2003, Koenig, 1950, Moody and Attard, 2003, Schmelzer and Baidakov, 2001, Schmelzer and Baidakov, 2003, Schmelzer et al., 2006). Nonclassical methods predict a key impact of second-order effects in the curvature dependence of the surface tension (represented by the rigidity coefficient) for tiny clusters. The deviation of the properties of the critical cluster of the newly evolving phase from that of its bulk macrophase might be explained by the assumption, that the critical cluster

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is less ordered than the corresponding bulk phase (e.g., Fokin et al., 2000). In the present case, the authors applied advanced MD simulations to determine the rigidity coefficient. A negative deviation of the surface tension from its bulk property (CPA) leads to a dramatic decrease of the thermodynamic barrier to form a critical embryo of the new phase (ice) for clusters of nanometric size, and consequently, to an dramatic enhancement of the nucleation rate.

3. The possibility of homogeneous nucleation of ice nano-particles in the polar summer mesosphere is a substantial conclusion.

4. The scientific approach and applied methods are valid. The results are discussed in an appropriate and balanced way. Related works are considered, references are appropriate.

5. The scientific results and conclusions are presented in a clear, concise, and well-structured way. Number and quality of figures/tables as well as use of English language are appropriate.

6. The description of experiments and calculations is sufficiently complete and precise to allow their reproduction by fellow scientists. With respect to the reproducibility of molecular dynamics simulations, of course, model setup, parameter configuration etc. would have to be disclosed (but not deserved to be part of the manuscript).

7. The authors give proper credit to related work and clearly indicate their own new/original contribution. But I recommed to include into the reference list also the review paper of Rapp and Lübken (2004).

8. The title clearly reflects the contents of the paper.

9. The abstract provides a concise and complete summary.

10. The overall presentation is well structured and clear.
11. The language is fluent and precise. Minor comments:
    - Page 14503, lines 6–9: Please replace brackets and commas for clearance.
    - Page 14505, line 11: "Where, $C \approx 373 \ldots$". Please restructurise this sentence and consider annotation of units.
12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?
    - No. See comments on Eqs. 2 and 4 with respect to units and annotation in my initial quick report on the manuscript.
13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?
    - See comments on Figs. 3 and 5 in my initial quick report on the manuscript.
14. The number and quality of references are appropriate.
15. The amount and quality of supplementary material is appropriate.

3 Technical corrections

The paper should be subject of technical revision (e.g., unification of citation style in both text and reference list, punctuation, case insensitivity).

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